A STUDY OF ALPHA-SUBSTITUTED ACRYLATE POLYMERS AND COPOLYMERS

BY
LYNN BURRITT WAKEFIELD
B.A., Reed College, 1936
M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942

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Introduction

The polymerization of ethyl α-bromoacrylate yields a product which when treated with potassium iodide in dioxane solution at room temperature, yields free iodine in an amount equivalent to from 5 to 30 percent of the bromine in the polymer; when the treatment is carried out at the boiling point of dioxane, 101°, from 80 to 96 percent of the bromine is replaced. These facts have been brought forward[1] as proof that haloacrylic acid polymers are of the "head to head" type, in contrast to the usual "head to tail" mode of vinyl polymerization.

Bromination of polyacrylyl chloride[2] with subsequent conversion to the ester gave a product which, although it contained about 44 percent of the theoretical amount of bromine, still reacted with potassium iodide in dioxane solution to give approximately one-half the theoretical amount of free iodine. This indicated that the presence of bromine in the starting material did not lead to a different type of polymer.

Discussion of Results

Repetition of the work of Marvel and Levesque[2] on the bromination of polyacrylyl chloride led to the preparation of a number of samples of polymers containing increased amounts of bromine; up to 70 percent of the theoretical was attained. Long periods of reaction, large excesses of bromine and elevated temperatures were employed without success in increasing the amount of bromine introduced. One sample of polymethyl α-chloroacrylate was prepared by chlorination of polyacrylyl chloride, which contained nearly 97 percent of the theoretical amount of chlorine; of this only about 20 percent was removable by potassium iodide ,whereas with the bromin-

ated samples from 40 to 60 percent of the bromine was replaced. Some doubt arose as to whether the entire magnitude of these figures corresponded to actual removal of halogen by potassium iodide; for the removal of some adjacent halogens would leave a double bond which, if the next polymeric unit were attached by a "head to tail" instead of a "head to head" linkage, would so activate the halogen in that unit that it could be removed by the action of heat alone. To test this point polyethyl α-bromoacrylate was treated at room temperature in dioxane solution with potassium iodide for several days, then separated from the iodide by precipitation in water and refluxed in dioxane solution alone. By the heat treatment the polymer lost some 60 percent of its bromine. This gives support to the belief that the structure of the bromoacrylate polymers is not exclusively "head to head" but partly "head to tail," for only such a combination of linkages would agree with the known fact that some of the bromine is removable by potassium iodide at room temperature and some may then be cracked out by heat alone. Figures obtained from treatment in acetone solutions at 25° indicate that at least 20 percent of the bromine is on adjacent carbon atoms.

Several copolymers made up of ethyl α-chloro- or α-bromoacrylate and ethyl acrylate, methyl methacrylate, styrene and acrylonitrile were treated with ammonia or potassium phthalimide but the products were found to be highly variable and no clear-cut reaction occurred. The reaction of dimethylamine with polyethyl α-bromoacrylate was smoother and led to a product containing considerable quantities of nitrogen, still somewhat short of theoretical, however.

Bibliography

1. Marvel and Cowan, J. Am. Chem. Soc., **61**, 3156 (1939).
2. Marvel and Levesque, **ibid.**, **61**, 3244 (1939).

VITA

The author was born in Creswell, Oregon on April 28, 1914. He attended grammar and high schools in Milwaukie, Oregon. Entering Reed College in 1932, he graduated in 1936 with the B. A. degree. From February, 1937 to July, 1938 he was employed as chemist by the Archer-Daniels-Midland Co., at Portland. In September, 1938 he entered the Graduate School of the University of Illinois and was granted the M. S. degree by that institution in June, 1939. During the years 1939-1941 he was employed as special research assistant in the Agricultural Experiment Station, while studying for the degree of Doctor of Philosophy in Chemistry.

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